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Survey Analysis of Phenolic Compounds in Industrial Effluents by Gas Chromatography-Mass Spectrometry

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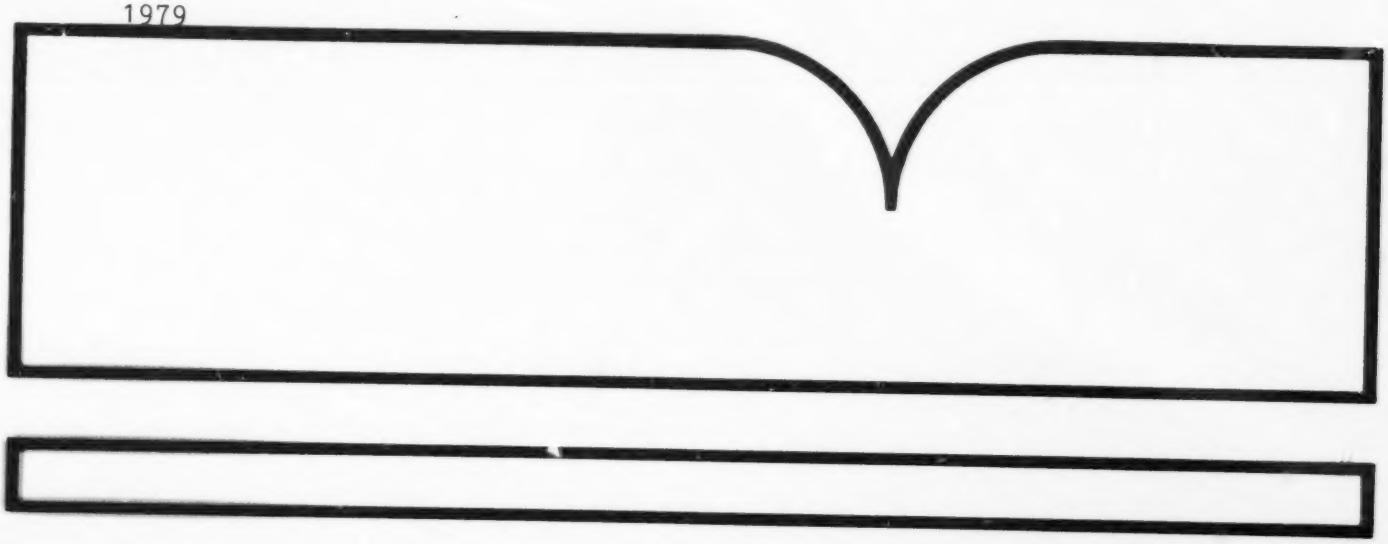

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16. ABSTRACT

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JOURNAL ARTICLE

W. M. Shackelford[1] *and R. G. Webb*[1,2]

Survey Analysis of Phenolic Compounds in Industrial Effluents by Gas Chromatography—Mass Spectrometry[3]

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ABSTRACT: Analyzing industrial effluents for phenolic compounds involves a number of problems both in the separation of these compounds from the aqueous medium and in the chromatography of the extracted compounds. Use of a continuous liquid–liquid extractor improved the recovery of phenolic compounds from those effluents that formed intractable emulsions during liquid–liquid extraction by shake-out. Tenax GC and SP-1240 DA proved to be the best general-purpose gas chromatographic column packings for a broad range of phenolic compounds. Derivatization procedures using diazomethane and pentafluorobenzyl bromide were found to be successful only under rigorously controlled conditions. For survey work, it appears that derivatization is of questionable value for initial qualitative analysis, because is many cases, the character of the matrix is not known.

KEY WORDS: phenols, gas chromatography–mass spectrometry, extraction, derivatization

Existing federal legislation as well as the Environmental Protection Agency (EPA) Natural Resources Defense Council Consent Decree of June 1976 require assessment of effluents from 21 industrial categories for specific phenolic compounds. Additionally, municipal sewage treatment plants are to be surveyed in the near future. The magnitude of the analytical problem for such an analysis program is staggering when one considers the variety of sample matrices and the dynamic range of concentrations both in different industrial effluents and in untreated and treated wastes. The purpose of this work, then, was to provide

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[2]Deceased 12 Jan. 1978.
[3]Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

a series of analysis modules that, depending upon the dictates of the sample, could be assembled for the survey analysis of effluents for phenolic compounds without serious perturbation to the rest of the sample.

Gas chromatography–mass spectrometry (GC–MS) was the technique chosen for this group of survey analyses because of its sensitivity and because of its ability to identify unknown compounds from their fragmentation patterns. Although gas chromatography alone can be used to monitor the levels of known components once an effluent has been characterized, initial survey requires a detector capable of identifying individual components. Computerized mass spectrometry was the choice for such a detector, because many laboratories use it routinely, and large collections of standard spectra exist for computer-aided identification of unknowns.

A glance at most untreated effluents is enough to convince the casual observer that organic analysis will be a difficult task. The problem is compounded by the fact that, in order to clean up the specimen for analysis, some components may be sacrificed.

Separation of phenolic compounds from water has been accomplished in other work by liquid–liquid extraction [*1*],[4] accumulation on resins [*2*], and steam distillation followed by liquid–liquid extraction [*3*]. In all three separation methods, phenols are removed quantitatively from the aqueous medium. Accumulation and steam distillation, however, may cause losses of components other than phenols from the sample. Whereas steam distillation and resin accumulation have been shown to give good recovery of phenols selectively, it was decided in this work to use only liquid–liquid extraction techniques for recovery of a broader band of sample components.

Because the phenols are of sufficient polarity to present serious problems to gas chromatography, several column packings were evaluated with respect to elution of phenols. Derivitization of the phenols to form more easily chromatographed species was attempted to enhance further the chromatography of the species of interest.

Procedure

Equipment

GC–MS–Three systems–two quadrupoles and a magnetic sector instrument–produced essentially equivalent results in this study. A Finnigan 3200 mass spectrometer connected by a glass jet separator to a Varian 1200 gas chromatograph was used to run standards as well as samples from the tanning industry. A System Industries System 150 data system was used for recording, storing, and analyzing data. A Varian MAT CH5 DF MS interfaced by a double-stage Watson-Biemann separator to a Varian 1400 gas chromatograph was used for standards runs as well as for samples from the wood products industry. Samples from a textile dye plant and appropriate standards were run on a Varian MAT 44 GC–MS

[4]The italic numbers in brackets refer to the list of references appended to this paper.

system employing a glass jet separator as the interface. Both Varian instruments were interfaced to a Varian SS-144 data system for recording, storing, and analyzing test results.

GC Columns—All chromatographic columns were 1.8-m, 2-mm inside diameter coiled glass tubing. Packing materials were held at both ends of the columns with plugs of silanized glass wool. Column packings used in this work were 1 percent SP-2250 on 100–120 mesh Supelcoport, 80–100 mesh Tenax GC, 1 percent SP-1240 DA on 100–120 mesh Supelcoport, 1 percent SP-1000 on 100–120 mesh Supelcoport, and 80–100 mesh Ultra-Bond 20M.

Extraction Apparatus—Liquid–liquid extractions performed using shake-out techniques were done in 2-litre separatory funnels with Teflon stopcocks. Continuous liquid–liquid extractions were performed with either of two heavier-than-water extractors. The first was a 4-litre capacity extractor obtained from Aldrich (catalog no. 157-5). An alternate extractor of slightly different design was the Hershberg-Wolf extractor obtained from Ace Glass (catalog no. 6841). After extraction by shake-out or continuous extraction, concentration of the extract was accomplished using Kuderna-Danish apparatus [*4*].

Chemicals—Standards of eleven phenolic compounds were procured commercially and, after checking the purity by GC, were used without further purification. Methylene chloride was distilled-in-glass grade from Burdick and Jackson.

Specimen Preparation

Samples from the three industries tested were stored at 4°C until actual extraction. At the start of the analysis procedure, the samples were mechanically stirred to assure some measure of homogeneity. The effect of filtering off suspended solids, or their behavior in the extraction procedure, is largely unknown at this time. A 1- or 2-litre sample (a 2-litre sample could be used only in the Aldrich 4-litre continuous extractor) was measured into a graduated cylinder and transferred to the separatory funnel or continuous extractor. The cylinder was washed with several portions of the final volume of extracting solvent. Because the analyses being run were surveys, both an acidic and a basic extraction were performed. Initially, the specimen was adjusted to pH 11 or higher and an extraction was performed. The resultant aqueous portion was then adjusted to pH 2 or lower and a second extraction performed. The final aqueous portion was then discarded.

Both the acidic and basic shake-out extractions were performed with three portions each of methylene chloride. A total of 400 ml of solvent was used for each of the two fractions. In the case of emulsion formation, recovery of 85 percent of the solvent volume used was considered indicative of a satisfactorily broken emulsion. Procedures used for breaking emulsions were glass wool filtration, centrifugation, and settling for protracted periods.

The acidic and basic continuous extractions were performed by charging the apparatus with an appropriate volume of sample (1 or 2 litres) and providing an

appropriate volume of methylene chloride in the solvent reservoir (300 to 500 ml). Refluxing was carried out for a period of 24 h. Recovery of 85 percent of the solvent was deemed indicative of a satisfactory extraction as in the case of shake-out extractions.

The methylene chloride extracts were concentrated to a final volume of 1 ml by Kuderna-Danish evaporation. Initial evaporation to a volume of 5 to 10 ml was accomplished using a three-ball macro-Snyder column and a 10-ml graduated receiver tube. Further evaporation was accomplished by attaching a two-chambered micro-Snyder column to the receiver tube and carefully monitoring the distillation until the final volume of 1 ml was reached. At this point, the acid extractable fraction of the specimen was ready for either direct injection into the GC–MS or derivatization and subsequent injection. Specimen extracts were stored in 2-ml serum vials with crimped caps that were lined with Teflon-coated rubber. Those specimen extracts not used immediately were stored in a freezer.

Techniques

GC–MS–Table 1 lists the parameters associated with gas chromatography in this work. Injection volumes were limited to 2 $\mu\ell$ or less depending upon the concentration of organic material in the extract. The MS parameters were optimized for each run with ionization energy being 70 eV throughout. Scan times were set to approximately 4 s so that small peaks eluting from packed columns (12 to 15 s duration) would have a minimum of three scans per peak.

TABLE 1–*Gas chromatographic parameters.*

Column	Injector Temperature, °C	Temperature Program, °C	Carrier Gas, helium ml/min	Separator Temperature, °C
SP-2250	275	70–270 at 6°/min	30	275
SP-1000	225	70–250 at 8°/min	30	275
Ultra-Bond	225	70–240 at 8°/min	30	275
SP-1240 DA	225	70–200 at 10°/min	30	275
Tenax-GC	225	180–300 at 8°/min	30	275

Methylation–Methylation of the extracts with diazomethane was done according to the method of Webb et al [*4*]. Modification of the method was avoided except at the end of the reaction time. At this time the reaction mixture was purged with nitrogen or a drop of acetic acid was added to quench the reaction.

Pentafluorobenzyl Ether Formation–Derivatization of phenols by the formation of pentafluorobenzyl ether was attempted both by the method of Kawahara [*5,6*] and that of Davis [*7*].

Experimental Results

GC Column Evaluation

Selection of a GC column for separating the components in the phenol-bearing extract depended principally upon whether the column would allow elution of all eleven model compounds. The models were chosen from EPA's list of priority pollutants [*8*]. Table 2 shows the elution ability (results obtained for each of the columns tested) of each of the columns tried with respect to the eleven model compounds. Tenax GC and SP-1240 DA were the only two column packings tested that met the eleven-compound elution criterion. None of the other columns tried would elute 2,4-dinitrophenol or 4,6-dinitro-2-cresol at even the 1000 ng level. In Table 3 can be seen the elution orders and relative retention times of the model compounds on both Tenax GC and SP-1240 DA as referenced to 2-nitrophenol.

TABLE 2—*Performance of selected chromatographic columns for elution of eleven phenols.*

Compound	SP-2250	SP-1000	Ultra-Bond	SP-1240 DA	Tenax GC
Phenol	yes	yes	yes	yes	yes
2-Chlorophenol	yes	yes	yes	yes	yes
2-Nitrophenol	yes	yes	yes	yes	yes
4-Chloro-3-cresol	yes	yes	yes	yes	yes
2,4-Dichlorophenol	yes	yes	yes	yes	yes
2,4-Dimethylphenol	yes	yes	yes	yes	yes
2,4,6-Trichlorophenol	yes	yes	yes	yes	yes
4,6-Dinitro-2-cresol	no	no	no	yes	yes
2,4-Dinitrophenol	no	no	no	yes	yes
Pentachlorophenol	poor	poor	poor	yes	yes
4-Nitrophenol	no	poor	poor	poor	poor

TABLE 3—*Relative retention times (RRT) for eleven phenols on Tenax GC and SP-1240 DA referenced to 2-nitrophenol.*

Tenax GC		SP-1240 DA	
Compound	RRT	Compound	RRT
Phenol	0.79	2-Chlorophenol	0.95
2-Chlorophenol	0.84	2-Nitrophenol	1.00
2-Nitrophenol	1.00	Phenol	1.08
2,4-Dimethylphenol	1.02	2,4-Dimethylphenol	1.15
2,4-Dichlorophenol	1.06	2,4-Dichlorophenol	1.17
4-Chloro-3-cresol	1.27	2,4,6-Trichlorophenol	1.31
2,4,6-Trichlorophenol	1.34	4-Chloro-3-cresol	1.43
2,4-Dinitrophenol	1.68	2,4-Dinitrophenol	1.87
4-Nitrophenol	1.73	4,6-Dinitro-2-cresol	1.95
4,6-Dinitro-2-cresol	1.82	Pentachlorophenol	2.36
Pentachlorophenol	2.01	4-Nitrophenol	3.40

The objective level of detection was set at 100 ng per injection, which corresponds to a sample concentration of about 50 ppb.

Both Tenax GC and SP-1240 DA have characteristics that keep them from being perfect, however. Tenax GC tends to harden into an impenetrable plug after a few heat–cool cycles. It was virtually impossible to repack a column, because the hardened Tenax GC could not be removed. It was found, however, that if a Tenax GC column were allowed to remain at temperatures above 150°C without cooling to room temperature, column life could be prolonged indefinitely. SP-1240 DA, on the other hand, cannot be taken to temperatures above 200°C and cannot be exposed to basic compounds in the injected sample without adversely affecting performance. Within these limits, however, SP-1240 DA was found to be quite satisfactory.

Figures 1 and 2 depict chromatograms of the eleven phenols run on Tenax GC and SP-1240 DA, respectively, using MS as the detector.

Phase Separations

Phenolic compounds were separated from the aqueous sample by liquid–liquid extraction as described above. The relative merits of shake-out and continuous extraction were judged strictly on the basis of recovery of the eleven model compounds from spiked solutions.

As shown in Table 4, only minor differences between the techniques are exhibited in the recoveries of the model compounds from spiked distilled water. This

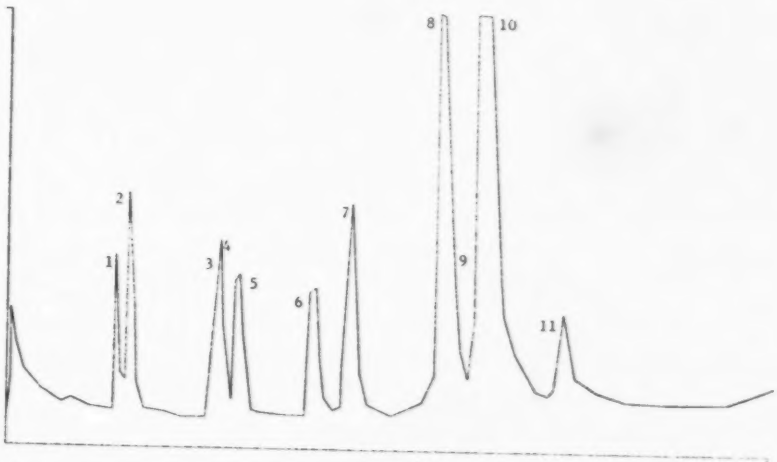


FIG. 1—*Eleven-phenol standard chromatographed on a 1.8-m Tenax GC column. Numbered peaks are: phenol (1), 2-chlorophenol (2), 2-nitrophenol (3), 2,4-dimethylphenol (4), 2,4-dichlorophenol (5), 4-chloro-3-cresol (6), 2,4,6-trichlorophenol (7), 2,4-dinitrophenol (8), 4-nitrophenol (9), 4,6-dinitro-2-cresol (10), pentachlorophenol (11). All components were 100 ng per injection except 8 and 10, which were 1000 ng per injection.*

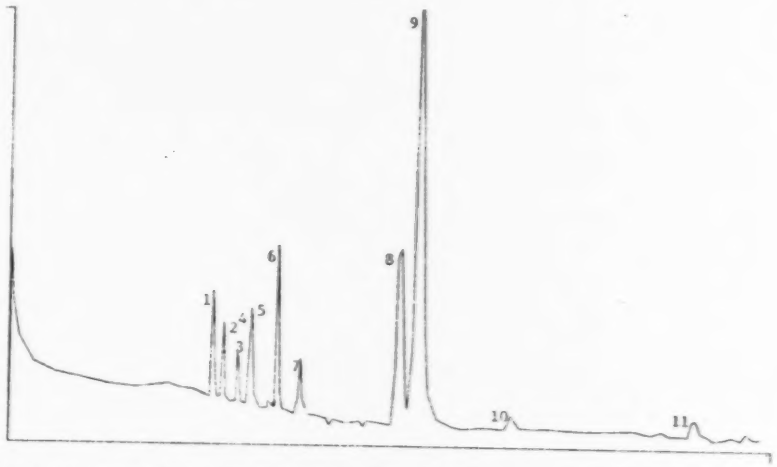


FIG. 2—*Eleven-phenol standard chromatographed on a 1.8-m SP-1240 DA column. Numbered peaks are: 2-chlorophenol (1), 2-nitrophenol (2), phenol (3), 2,4-dimethylphenol (4), 2,4-dichlorophenol (5), 2,4,6-trichlorophenol (6), 4-chloro-3-cresol (7), 2,4-dinitrophenol (8), 4,6-dinitro-2-cresol (9), pentachlorophenol (10), 4-nitrophenol (11). All components were 100 ng per injection except 8 and 9, which were 1000 ng per injection.*

TABLE 4—*Recovery of 100 μg/litre spikes of the eleven phenols from distilled water by shake-out and continuous extraction.*

Compound	Shake-out, Percent Recovery	Continuous Extraction, Percent Recovery
Phenol	73	67
2-Chlorophenol	92	93
2-Nitrophenol	91	95
4-Nitrophenol	90	95
2,4-Dichlorophenol	76	78
2,4-Dimethylphenol	79	75
4-Chloro-3-cresol	80	87
2,4,6-Trichlorophenol	78	82
2,4-Dinitrophenol	91	83
4,6-Dinitro-2-cresol	97	96
Pentachlorophenol	93	91

result was expected, because both techniques have been used for extraction for years.

The data for an actual effluent, however, indicate that where interferences that hamper good phase separation are present, continuous extraction appears to be more efficient. Moreover, phase separation in some samples was so poor that only continuous extraction was used.

Table 5 gives the recoveries of the phenols from a spiked sample of the untreated effluent from a textile dye plant. Except for two compounds, 2-nitro-

TABLE 5—*Comparison of recovery of 100 μg/litre spikes of phenols from a textile dye effluent by continuous extraction and shake-out.*

Compound	Shake-out, Percent Recovery	Continuous Extraction, Percent Recovery
Phenol	...[a]	...[a]
2-Chlorophenol	44	74
2-Nitrophenol	54	64
4-Nitrophenol	...[a]	...[a]
2,4-Dichlorophenol	51	64
2,4-Dimethylphenol	43	56
4-Chloro-3-cresol	60	75
2,4,6-Trichlorophenol	72	74
2,4-Dinitrophenol	...[a]	...[a]
4,6-Dinitro-2-cresol	58	104
Pentachlorophenol	28	44

[a]Present in sample.

phenol and 2,4,6-trichlorophenol, the continuous extractor shows a greater than 10 percent advantage in recovery. It is postulated that the differences in recoveries reflect the loss of components during the emulsion-breaking steps required in shake-out.

Emulsion problems associated with samples collected from the wood preserving industry and the tanning industry were so severe during shake-out that the continuous extractor was used exclusively. Although recoveries of spikes were not good in these samples, detectable amounts were recovered from 100 μg/litre spikes. In the three effluents that were analyzed, the phenols actually present in the sample were at levels 10 to 100 times greater than the spikes.

Derivatizations

Two types of derivatives were made to attempt to ease chromatographic problems with the polar phenols. Methyl ethers of the phenols (anisoles) were synthesized using diazomethane, and pentafluorobenzyl ethers were made using pentafluorobenzyl bromide. Both derivatization methods, although encouraging when used on single standards, were disappointing when applied to mixtures of the standards and to spiked effluents.

Diazomethane—When reacted singly with diazomethane, each of the phenols was converted to the corresponding anisole with 90 percent or better yield as quantified by standard addition. As may be expected, different reaction times were required for each compound. Because the work was directed toward survey of unknown samples, no attempt was made to quantify these times. It was found, however, that phenol took the longest time to react; 10 min past the time of solution coloring as called for in the method [*4*]. When examination of derivatization mixtures began, it was found that by the time phenol had been quantitatively changed to anisole, loss of other anisoles had occurred. On the

other hand, incomplete methylation occurred when methylation was stopped after a shorter time. Figure 3 shows the results of what was considered an optimum methylation of the eleven-phenol mixture at a concentration of 50 $\mu g/\mu\ell$ each. As can be seen, anisole was poorly recovered. Dimethylanisole was not recovered, but the other nine anisoles were recovered in varying yields.

In the methylation of a textile dye effluent sample extract, even more problems arose when trying to ensure optimum reaction times. Because the specimen was known to contain large amounts of phenol and 2,3-dimethylphenol, methylation was carried out for 15 min. The phenol and dimethylphenols were methylated in good yield, but the more acidic phenols–2,4-dinitrophenol, 2-nitrophenol, and 4-nitrophenol–were lost. Thus, the underivatized specimen gave better qualitative information.

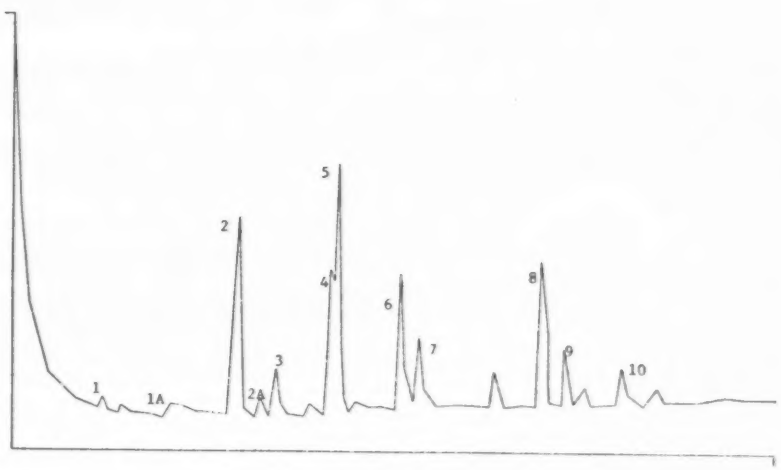
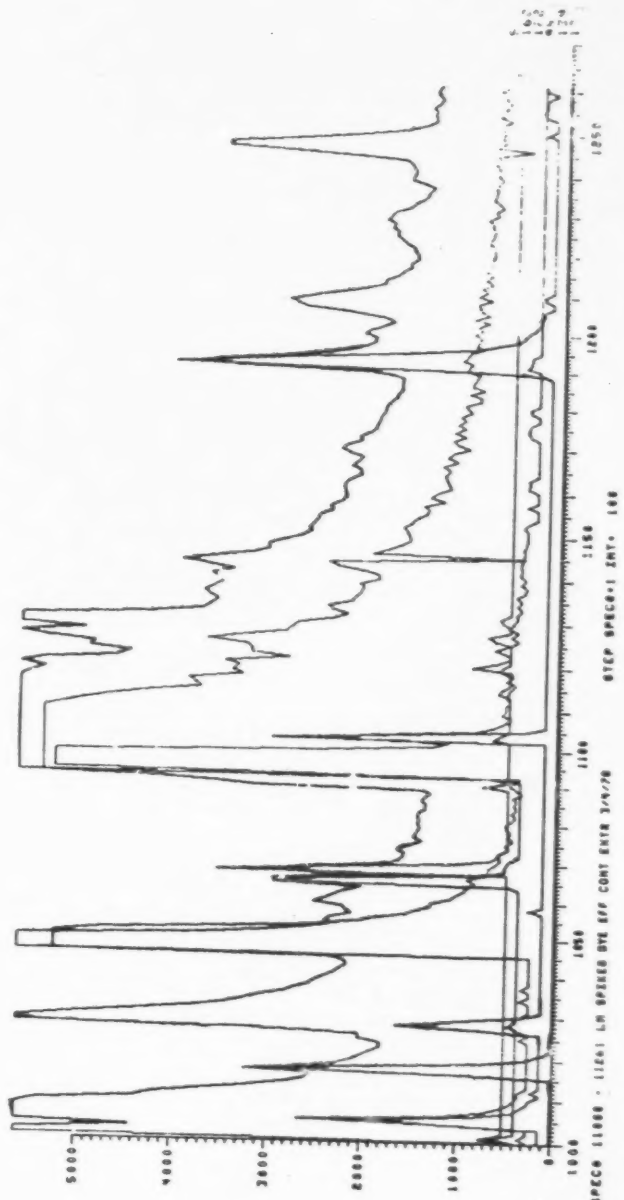


FIG. 3–*Methylation results for eleven-phenol standard run on an SP-2250 column. Numbered peaks are: anisole (1), phenol (1A), 2-chloroanisole (2), 2-chlorophenol (2A), 4-chloro-3-methylanisole (3), 2,4-dichloroanisole (4), 2,4,6-trichloranisole (5), 2-nitroanisole (6), 4-nitroanisole (7), pentachloroanisole (8), 4,6-dinitro-2-methylanisole (9), 2,4-dinitroanisole (10).*

Pentafluorobenzylation–Derivatization by forming the pentafluorobenzyl ether analogs of the phenols was extremely time consuming by the method of Kawahara [*5,6*]. Using the method of Davis [*7*] required less time, but for dimethylphenol, it still required 2 h. The nitrophenols reacted in less than 1 h and were easily chromatographed. It was judged, however, that pentafluorobenzylation would suffer the same drawbacks as methylation in an actual sample, with the exception that no evidence of reagent-induced sample component breakdown was seen using the Davis or Kawahara methods.



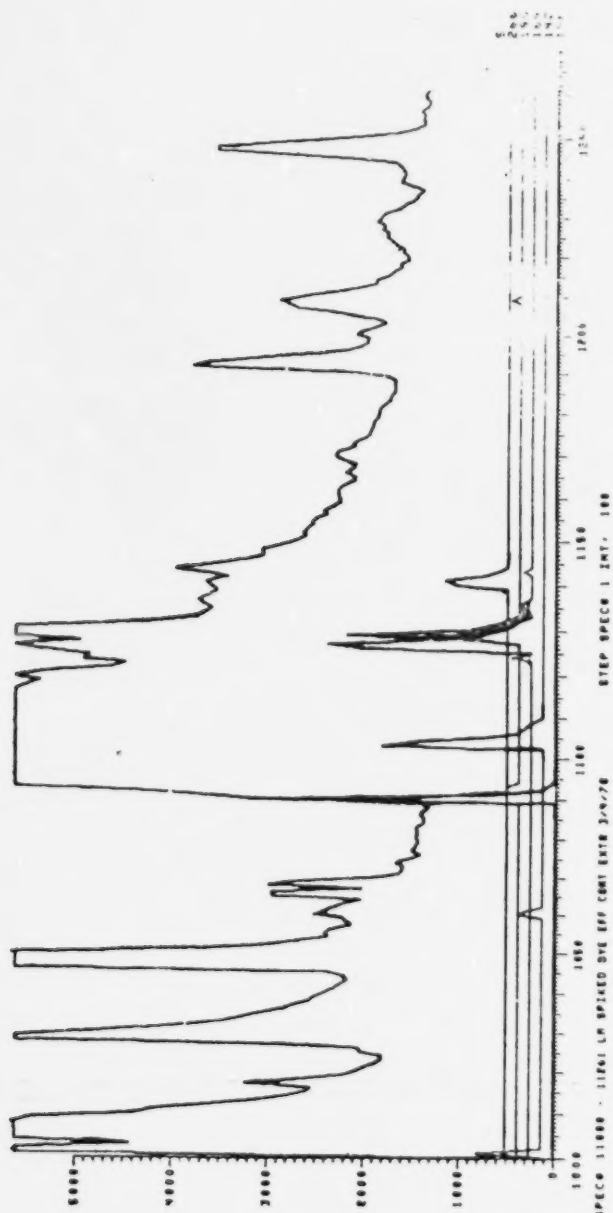
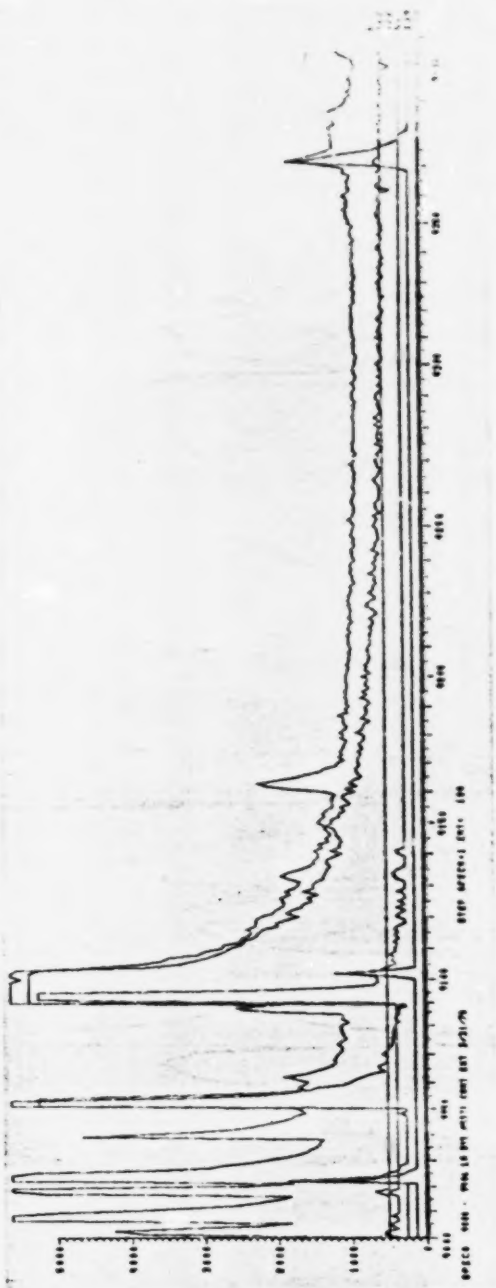


FIG. 4—*Textile dye plant effluent spiked with 100 ppb each of eleven phenols. Traces are labeled with the molecular ions given in Table 6.*



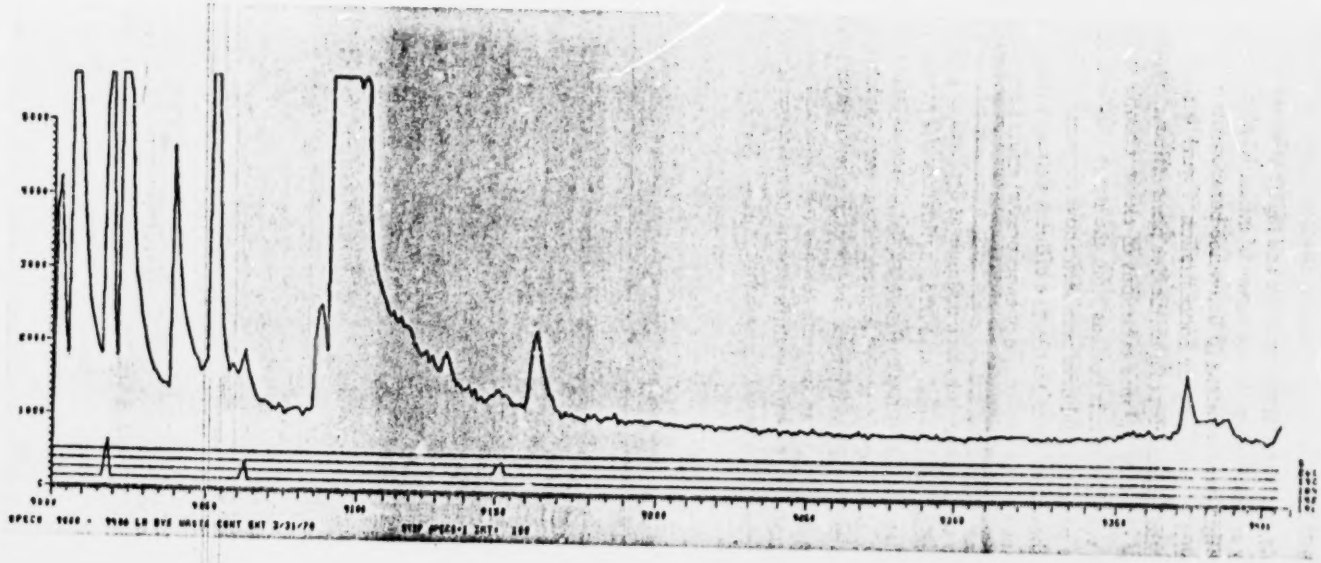


FIG. 5—*Textile dye plant effluent, unspiked. Traces are labeled with the molecular ions given in Table 6.*

Mass Spectrometry

Use of the mass spectrometer as a sensitive and highly selective detector for gas chromatography is well known. In the survey of industrial effluents for phenols, MS is an especially effective means to determine components of interest among other components of much higher concentration. Figure 4 shows a total ion current plot for the acid extract of a textile dye plant effluent. Superimposed on this plot are the plots for the molecular ions of eleven phenols spiked into the effluent before extraction. It is obvious from the figure that without MS data, only two of the phenols could have been seen above the noise of the sample matrix. Figure 5 shows the same textile dye effluent extract without the eleven-phenol spike. Again, only two of the phenols present could have been seen with conventional GC detectors.

Quantification of the phenols in such a sample as depicted in Figs. 4 and 5 was accomplished using an internal standard, anthracene-d_{10}. Relative response ratios of the phenols to anthracene-d_{10} were calculated in standard runs, and these ratios were then applied to the extracts of interest. Table 6 gives the relative response ratio of the most intense ion of each phenol to the most intense ion of anthracene-d_{10}. As can be seen, there is much disparity in these ratios. Most of the disparity is due to the difficulty in chromatographing the dinitrophenols, *p*-nitrophenol and pentachlorophenol.

TABLE 6—*Relative mass spectrometer responses of eleven phenols compared to anthracene-*d_{10}.

Compound	Ion Measured	Relative Response
Phenol	94	0.9
2-Chlorophenol	128	1.1
2-Nitrophenol	139	2.5
4-Nitrophenol	139	17
2,4-Dichlorophenol	162	2.0
2,4-Dimethylphenol	122	1.6
4-Chloro-3-cresol	142	2.3
2,4,6-Trichlorophenol	196	4.1
2,4-Dinitrophenol	184	26
4,6-Dinitro-2-cresol	198	11
Pentachlorophenol	266	27
Anthracene-d_{10}	188	1.0

Conclusions

It has been shown that often-used techniques for analyzing water samples for phenols have strenghts and weaknesses that become critical depending upon whether analysis is directed at some particular component in the sample or is directed at all components of the sample. For survey analysis for phenolic compounds, compromises must be made that may lessen the sensitivity for one or more components yet heighten the overall sensitivity as far as numbers of de-

tected components are concerned. Because of such compromises, the quantification of single components is extremely risky until after the survey analysis is complete.

For the survey analysis of phenolic compounds, it is apparent from the data presented here that the most accurate way of identifying components is the use of GC–MS to view as unperturbed a sample as possible. Derivatization, although easing some chromatographic problems, further removes the analyst from the sample. Finally, detection must be accomplished by a highly discriminatory technique, such as MS, if an unknown mixture is to be resolved.

References

[1] Matsumoto, G., Ishiwatari, R., and Hanya, T., *Water Research*, Vol. 11, No. 8, 1977, pp. 693–698.
[2] Criswell, C., Chang, R., and Fritz, J., *Analytical Chemistry*, Vol. 47, No. 8, 1975, pp. 1325–1329.
[3] *Standard Methods for Examination of Water and Wastewater*, 13th ed., American Public Health Association, New York, 1975, p. 502.
[4] Webb, R. G., Garrison, A. W., Keith, L. H., and McGuire, J. M., "Current Practices in GC-MS Analysis of Organics in Water," EPA-R2-73-277, U.S. Environmental Protection Agency, Washington, D.C., Aug. 1973.
[5] Kawahara, F. K., *Analytical Chemistry*, Vol. 40, No. 6, 1968, pp. 1009–1010.
[6] Kawahara, F. K., *Analytical Chemistry*, Vol. 40, No. 13, 1968, pp. 2073–2075.
[7] Davis, B., *Analytical Chemistry*, Vol. 49, No. 6, 1977, pp. 832–834.
[8] *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants*, U.S. Environmental Protection Agency, Washington, D.C., April 1977.